Equilibrium dec 17 file 2

Tuesday, 20 December 2022 13:37

Buffer Index and Buffer Capacity

(β) Buffer Index ⇒ Differential ratio of increase in amount of Strong Acid or strong Base added to the pH variation.

$$\beta = \frac{dn}{d(pH)} = \frac{\text{Small increase in moles of S.A or S.B}}{\text{Small pH Variation}}$$

$$= \frac{\Delta n}{\Delta pH}$$ → Total moles of S.A or S.B added

$$\boxed{\beta = \frac{\Delta n}{\Delta(pH)} \approx 2.303\frac{(c \cdot s)}{(c+s)}}$$

c = Conc. of Weak acid or weak Base in Buffer

s = Conc. of Salt Cation or salt anion in Buffer.

Qe What is Buffer index or capacity of

$\boxed{0.1M\ NH_4OH + 0.1M\ NH_4Cl}$

Sol^n

$$\beta = 2.303\frac{(c \cdot s)}{(c+s)}$$

$$\boxed{\beta = 2.303\left(\frac{0.1 \times 0.1}{0.1 + 0.1}\right) = 0.115}$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = x$$

- x<0.1 or 10^-1
  - Conc. of W.A >> Anion
  - Anion will be ignored
  - pH will be calculated only taking weak Acid
  - $pH = \frac{1}{2}[pKa - \log \textcircled{c}]$ → Conc. of W.A
- 0.1 ≤ x ≤ 10 (or 1/10)
  - Buffer will work
  - $pH = pKa + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$
- (x>10)
  - WA is ignored
  - $[CH_3COO^-] >>> [CH_3COOH]$
  - CH_3COO^- Hydrolysis is dominating
  - $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \textcircled{OH^-}$
  - Basic
  - $\boxed{pH = 7 + \frac{1}{2}[pKa + \log \textcircled{c}]}$ → Conc. of CH_3COO^-

Max Buffer Capacity is achieved when

[Salt Anion] = [W.A]

[Salt Cation] = [W.B]

Note:- $\boxed{\text{Buffer Capacity } (\beta)}$ → minimum amount (moles) of S.A or S.B added to 1 L Buffer to change its pH by 1 unit.

Δn moles of S.A added → ΔpH change is observed for 1 L Buffer

$$\boxed{\beta = \frac{\Delta n}{\Delta pH}}$$ ← 1 unit change in pH

Buffer Capacity

If $\boxed{\beta = 0.115}$ ⇒ It means 0.115 moles of S.A or S.B can be added to 1 L Buffer for 1 unit pH change.

↳ pH ↑ by 1 unit or pH ↓ by 1 unit

Buffer Range ⇒ pH Range in which Buffer will work effectively.

$\boxed{pH = pKa \pm 1}$ for Acidic Buffer

min pH: pKa − 1 = pH

max pH upto which Buffer will work like Buffer. pH = pKa + 1

$(pH)_{min} = pKa - 1$ —— pH of Buffer —— $(pH)_{max} = pKa + \textcircled{1}$

2 units diff.

$$\frac{[S]}{[C]} = \frac{1}{10}$$

$$\boxed{\log\left(\frac{S}{C}\right) = -1}$$

$$\boxed{[C] = 10[S]}$$

$$\left(\frac{S}{C}\right) = 10$$

$$\boxed{\log\left(\frac{S}{C}\right) = 1}$$

Basic Buffer Range

$\boxed{pOH = pK_b \pm 1}$

$\boxed{pOH = pK_b + 1}$ → $\frac{[S]}{[C]} = 10$

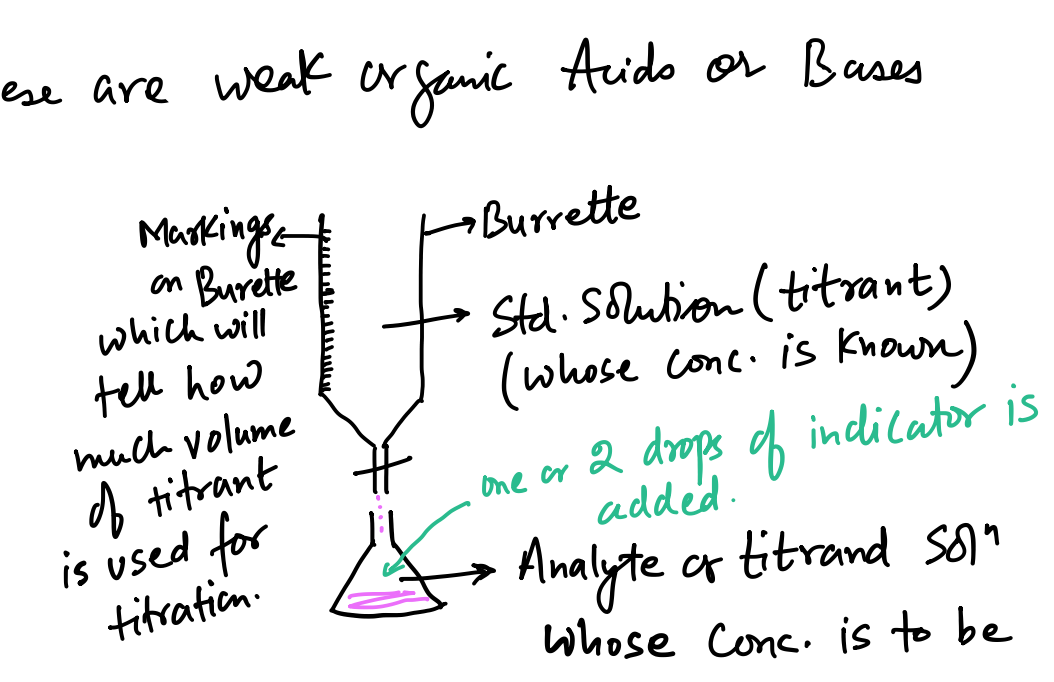
$\boxed{pOH = pK_b - 1}$ → $\frac{[S]}{[C]} = \frac{1}{10}$

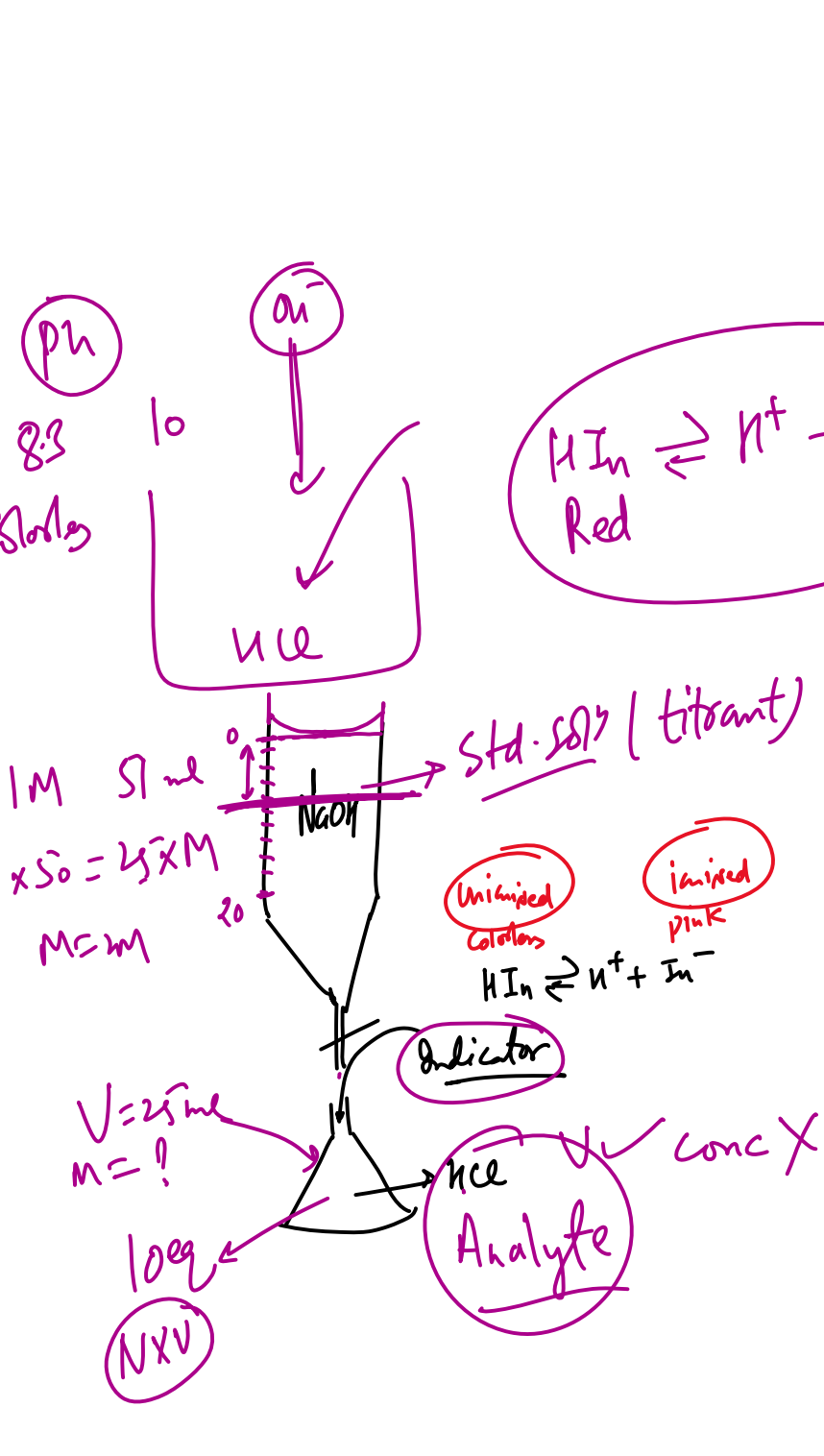
⊕ Indicators and Acid Base Titration

Indicators are those Substances which detect or indicate the end point in titration by color change.

↳ Rx^n b/w Acid & Base is already completed.

⇒ These are weak organic Acids or Bases


Markings on Burette which will tell how much volume of titrant is used for titration.
Burrette
Std. Solution (titrant) (whose conc. is known)
one or 2 drops of indicator is added.
Analyte or titrand Sol^n whose Conc. is to be determined.

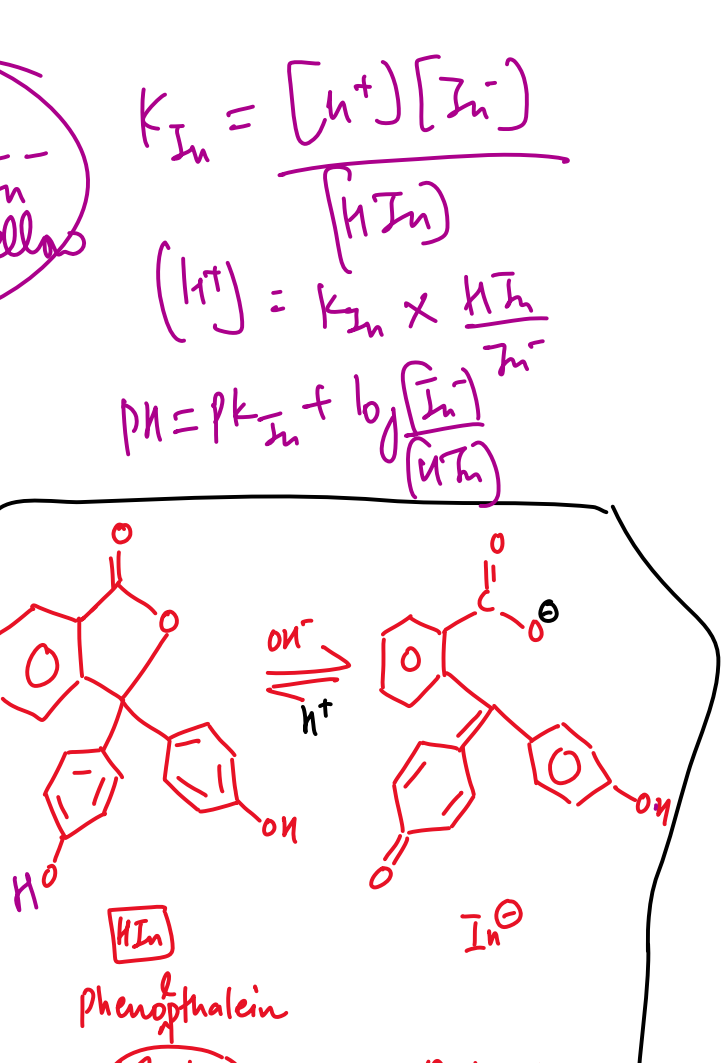


$$\boxed{HIn \rightleftharpoons H^+ + In^-}$$ Red, yellow

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

$$[H^+] = K_{In} \times \frac{HIn}{In^-}$$

$$pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$$



Equivalence point (Theoretical point)

Total analyte is completely Reacted with Std. Sol^n.

$\boxed{\text{equivalents of Analyte (or meq)} = \text{eq of titrant added from Burette}}$

⇓

$N_a V_a = N_t \textcircled{V_t}$

After equivalence point, one extra drop added to analyte Sol^n will bind with indicator and indicator show color change → Called as End point.

✓ To obtain almost accurate conc. (N or M) of analyte sol^n; end point & equivalence point must be very very close to each other i.e; Sol^n from Burette is added slowly (drop by drop).

⇒ Generally,

⇒ darker color is associated with Ionised part of indicator.

⇒ light color is associated with Unionised part.

eg. ① phenolphthalein indicator (ph) → Weak Acid

$$HPh \rightleftharpoons \overset{\text{Quinoid form}}{Ph^-} + H^{\oplus}$$

Unionised part: Colorless — Ionised part: Pink

In acidic medium, H⁺ is more, eq^m of indicator shifts Backward.

$\boxed{[HPh] > [Ph^-]}$

$\boxed{\text{Sol}^n \text{ will be Colorless}}$

In BASIC Medium OH⁻ is more, & these OH⁻ combine with H⁺; so that eq^m shifts forward; $\boxed{[Ph^-] > [HPh]}$

Pink color is observed.

② Methyl orange (MeOH) → Weak Base

$$MeOH \rightleftharpoons Me^+ + OH^-$$

Unionised: Yellow — Ionised: Red

Acidic Medium; H⁺ more & these H⁺ will react with OH⁻, Rx^n Shift forwards, Sol^n is Red

Basic Medium:- [MeOH] > [Me⁺]

Sol^n is yellow color

Note:- Color change of indicator is dependent on pH of Sol^n in which indicator is present.

pH of (indicator) → (In)

$$HIn \rightleftharpoons In^- + H^+$$

light Colored — Dark Colored

$$K_{eq} = K_{In} = \frac{[In^-][H^+]}{[HIn]}$$

In⁻ → Conj. Base

$$[H^+] = K_{In} \times \frac{[HIn]}{[In^-]}$$

$$\boxed{pH = pK_{In} + \log\frac{[In^-]}{[HIn]}}$$ In⁻ → Salt anion, HIn → Weak Acid

↳ Henderson-Hasselbach Eq^n

pH range for Indicator ⇒ It is the interval in which Indicator shows Color transition.

$\boxed{pH \text{ range} = pK_{In} \pm 1}$

min pH: $[In^-] < [HIn]$

$\boxed{10[In^-] = [HIn]}$

↳ $\boxed{pH = pK_{In} - 1}$

Sol^n is light colored

max pH: ↳ $[HIn] < [In^-]$

Sol^n will be dark colored.

eg. Phenolphthalein (ph)

↳ pH range ⇒ $\boxed{8.3 \text{ to } 10}$

$\boxed{\text{If pH of Sol}^n > 10}$ Sol^n is pink Colored.

$\boxed{\text{pH of Sol}^n < 8.3}$ → Sol^n is Colorless

pH ⇒ $\boxed{8.3 \text{ to } 10}$

↳ $\boxed{\text{Transition in color}}$ from Colorless to pink

$\boxed{MeOH}$ pH range ⇒ 3.1 to 4.4

$\boxed{pH < 3.1}$ ⇒ Red (ionised > unionised)

$\boxed{pH > 4.4}$ ⇒ Yellow (unionised > ionised)

$\boxed{pH = 3.1 \text{ to } 4.4}$ → transition ⇒ (orange Color)

$$\text{\% ionised part of indicator} = \frac{[In^-]}{[HIn] + [In^-]} \times 100$$

$$\text{\% unionised part} = \frac{[HIn]}{[HIn] + [In^-]} \times 100$$

Bromothymol Blue ⇒ $\boxed{\text{pH range} = (6 \text{ to } 7.6)}$

pH<6 ⇒ yellow

pH>7.6 ⇒ Blue

Methyl Red ⇒ $\boxed{4.2 \text{ to } 6.3}$

pH<4.2 ⇒ Red

pH>6.3 ⇒ Yellow

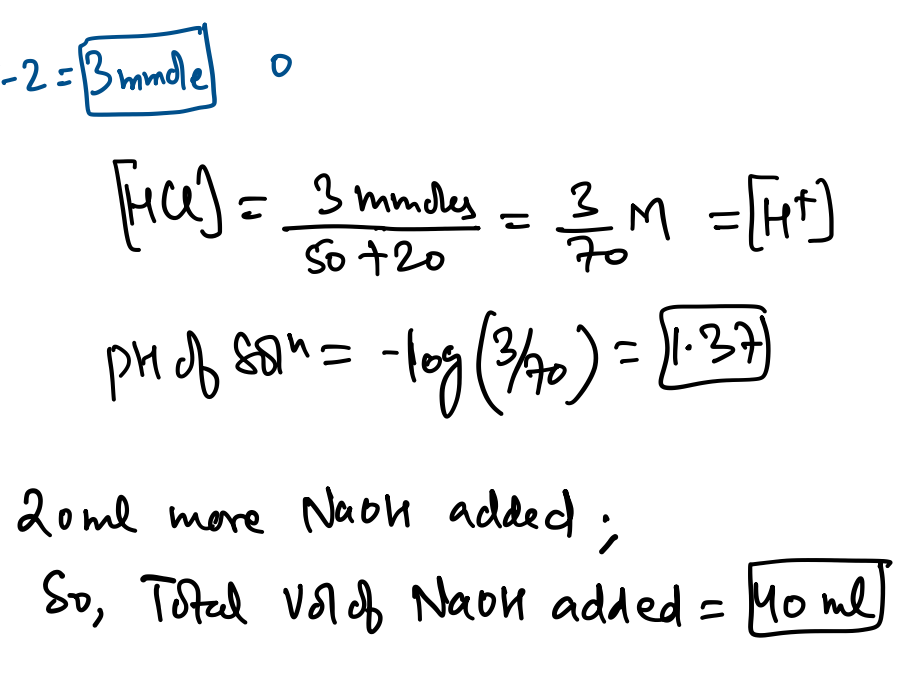
Selection of Indicator for Acid-Base Titration

① During A-B titr^n, there is a sudden change in pH near equivalence point due to extra amount added from Burette.

② The indicator will be suitable for given titr^n when pH range of indicator lie on sudden pH change limits.

③ For Best indicator, the mid point of pH range of indicator is pH of equivalence point.

⊕ Titration of S.Acid (Analyte) vs Str. Base (Std. Sol^n)



initial mmoles of HCl = 0.1 × 50 = $\boxed{5 \text{ mmoles}}$

(i) $V_{NaOH} = 0$ (No NaOH added)

pH of Sol^n = $-\log[H^+] = -\log(0.1) = 1$

(ii) $V_{NaOH} = 20ml$

$$HCl + \overset{0.1M}{NaOH} \longrightarrow \boxed{NaCl} + H_2O$$ (NaCl → Neutral salt)

HCl: 50 × 0.1 = 5mmole; NaOH: 20 × 0.1 = 2mmole

5 − 2 = $\boxed{3 \text{ mmole}}$; 0

$$[HCl] = \frac{3 \text{ mmoles}}{50 + 20} = \frac{3}{70}M = [H^+]$$

pH of Sol^n = $-\log(3/70) = \boxed{1.37}$

(iii) 20ml more NaOH added;

So, Total vol of NaOH added = $\boxed{40 \text{ ml}}$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

HCl: 5mmole; NaOH: 40 × 0.1

5 − 4 = $\boxed{1 \text{ mmole}}$; 4 − 4 = 0

$$[HCl]_{Resultant} = [H^+] = \frac{1}{90}M$$

$$pH = -\log\left(\frac{1}{90}\right) = 1.95$$

+9ml

(iv) $\boxed{V_{NaOH} = 49 \text{ ml}}$ ⇒ Total NaOH

$$[H^+] = \frac{5 - 4.9}{99} = \frac{0.1}{99}$$ $\boxed{pH = 3}$

+1ml

(v) $(V_{NaOH})_{Total} = 50ml$

$\boxed{\text{mmole HCl (or meq)} = \text{mmoles of NaOH (or meq)}}$ ⇒ Equivalence point

Complete neutralisation

Sol^n Neutral

$\boxed{pH = 7}$

+1ml

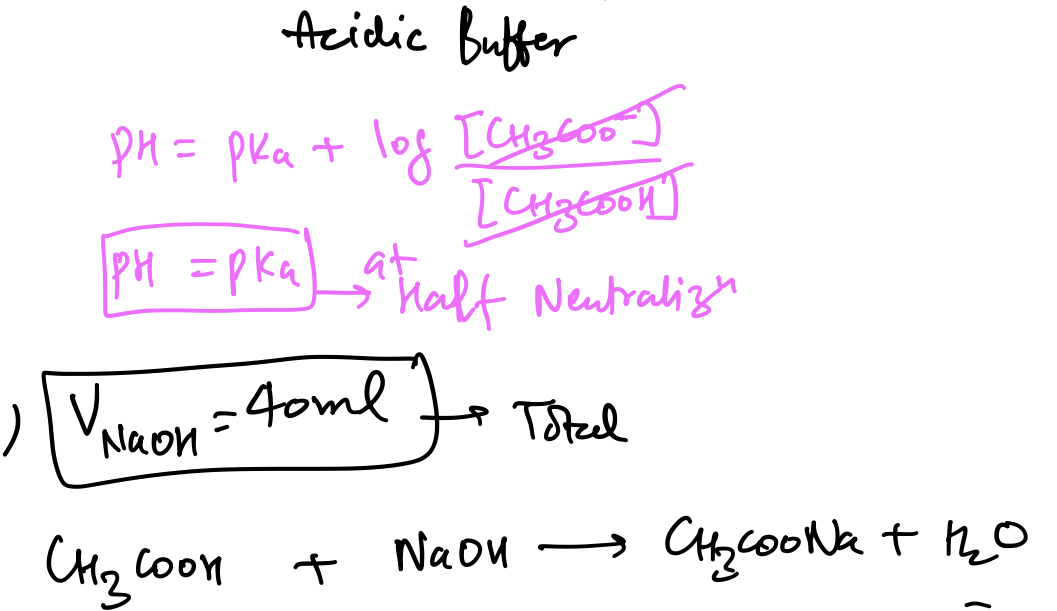
(vi) $(V_{NaOH})_{Total} = 51 ml$

0.1 × 1ml = 0.1 mmole Extra OH⁻ in Sol^n

$$[OH^-] = \frac{0.1}{101}M$$

pOH = 3 $\boxed{pH = 11}$

⊕ Titr^n of Weak Acid and Str. Base



i) $\boxed{V_{NaOH} = 0}$ Sol^n has only CH_3COOH (α ≤ 0.1)

+25ml

$$pH = \frac{1}{2}[pKa - \log c] = \frac{1}{2}[4.74 - \log 0.1] = 2.87$$

(ii) $V_{NaOH} = 25ml$

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

CH_3COOH: 50 × 0.1 ⇒ 5mmole; 5 − 2.5 = 2.5 mmole

NaOH: 25 × 0.1 = 2.5mmole; 0

CH_3COONa: 0; 2.5mmol

→ Half Neutraliz^n point

W.A + Salt of WA with S.B

Acidic Buffer

$$pH = pKa + \log\frac{\cancel{[CH_3COO^-]}}{\cancel{[CH_3COOH]}}$$

$\boxed{pH = pKa}$ → at Half Neutraliz^n

(iii) $\boxed{V_{NaOH} = 40ml}$ → Total

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

CH_3COOH: 5mmole; 5 − 4 = 1mmole

NaOH: 4 mmole; 4 − 4 = 0

CH_3COONa: —; 4 mmoles

$$\boxed{[CH_3COOH] = \frac{1}{90}M \quad [CH_3COONa] = \frac{4}{90}M}$$

↳ Buffer

$$\boxed{pH = pKa + \log\left(\frac{4}{1}\right) = \boxed{5.34}}$$

(iv) $V_{NaOH} = 49ml$

Buffer

$$pH = pKa + \log\left(\frac{4.9}{0.1}\right) = 6.44$$

(v) $\boxed{V_{NaOH} = 50ml}$

$$CH_3COOH + NaOH \longrightarrow \boxed{CH_3COONa} + H_2O$$ (CH_3COONa → BASIC Salt)

CH_3COOH: 5mmole; 0

NaOH: 5mmole; 0

CH_3COONa: —; 5mmole

$$\boxed{[CH_3COONa] = \frac{5}{100}M}$$

Salt Hydrolysis — Anionic Hydrolysis

$$\hookrightarrow pH = 7 + \frac{1}{2}[pKa + \log c]$$

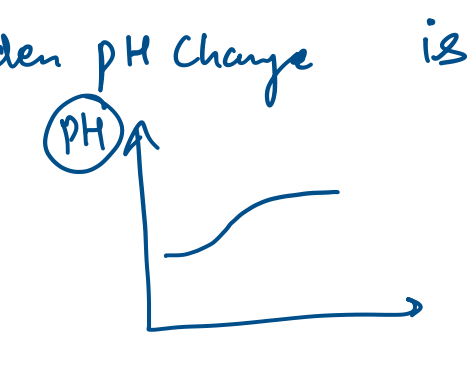
= 8.7 → at equivalence point

(vi) $V_{NaOH} = 51 ml$

$$[OH^-] = \frac{0.1}{101} \approx 10^{-3}$$

pOH = 3, $\boxed{pH = 11}$

⊕ Titr^n of Weak Acid & Weak Base

No suitable indicator is available, because sudden pH change is very small.